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PATENT  
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## Concentrated Surface-active Preparations

### Field of the Invention

This invention relates generally to surface-active substances and, more particularly, to water-based preparations of amphoteric or zwitterionic surfactants, more particularly betaines, which are distinguished by a low  
5 paste viscosity despite a high-active substance concentration.

### Prior Art

Amphoteric or zwitterionic surfactants are distinguished by excellent  
foam and cleaning properties coupled with excellent dermatological  
10 compatibility. Accordingly, they are used as important raw materials for the  
production both of detergents (for example manual dishwashing  
detergents) and of cosmetic preparations (for example hair shampoos).  
Within this group of compounds, alkyl betaines and preferably alkyl  
amidobetaines have acquired particular significance, the most important  
15 single product undoubtedly being cocamidopropyl betaine which is  
commercially available, for example, under the name of Dehyton® PK  
(Cognis).

Amphoteric or zwitterionic surfactants are marketed as water-based  
preparations, the interest of the manufacturer being directed towards  
20 marketing concentrates, i.e. reducing the quantity of water in the  
preparations to a minimum. However, there are limits to such a reduction  
because the active substance content cannot be increased at will because  
– depending on other ingredients – the surface-active substances begin to  
form a lamellar gel-form phase above a value of about 40% by weight. The  
25 extreme increase in viscosity which this involves and which, occasionally,  
only occurs during storage makes it virtually impossible to transport or  
pump the products. However, such products are unsuitable for marketing.

In the past, there has been no shortage of attempts to solve the problem of the increase in viscosity and gelation during storage. Such attempts have included in particular the addition of free fatty acids, optionally together with glycerol, which is proposed in European patent **EP 0560114 B1** (Goldschmidt). However, the disadvantage of this is that fatty acids are comparatively expensive additives and are not looked upon favorably in all end products subsequently produced and a measurable reduction in paste viscosity only occurs at values of 1 to 1.5% by weight. Alternatively, it is proposed in European patent **EP 0730572 B1** (Cognis) to reduce the viscosity by the addition of hydroxycarboxylic acids or salts thereof, more especially sodium citrate. Although smaller quantities are sufficient in this case, the price - which is still above that of fatty acids - makes the process relatively unattractive.

Accordingly, the problem addressed by the present invention was to provide new concentrated, water-based amphoteric or zwitterionic surfactant preparations which would be distinguished by a low Brookfield viscosity (20°C, spindle 1, 10 r.p.m.) of, in particular, less than 5,000 mPas for an active substance concentration of, for example, 25 to 55% by weight and which would not gel in storage.

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### **Description of the Invention**

The present invention relates to concentrated, low-viscosity surface-active preparations containing

- 25 (a) 25 to 50% by weight of amphoteric or zwitterionic surfactants and  
(b) 0.01 to 5% by weight of alkali metal sulfates,

with the proviso that the quantities add up to 100% by weight with water and optionally other electrolyte salts.

30 It has surprisingly been found that even the presence of very small

quantities of alkali metal sulfates, more especially sodium sulfate, is sufficient clearly to reduce the paste viscosity of highly concentrated water-based preparations of amphoteric or zwitterionic surfactants both by addition during production and by subsequent addition to the pastes. More particularly, even the unwanted effect of gradual gelation is reliably prevented.

#### Amphoteric surfactants

Examples of suitable amphoteric or zwitterionic surfactants are alkyl betaines, alkyl amidobetaines, aminopropionates, aminoglycinates, imidazolinium betaines and sulfobetaines. Examples of suitable alkyl betaines are the carboxyalkylation products of secondary and, in particular, tertiary amines corresponding to formula (I):



in which  $\text{R}^1$  represents alkyl and/or alkenyl groups containing 6 to 22 carbon atoms,  $\text{R}^2$  represents hydrogen or alkyl groups containing 1 to 4 carbon atoms,  $\text{R}^3$  represents alkyl groups containing 1 to 4 carbon atoms,  $q1$  is a number of 1 to 6 and Z is an alkali metal and/or alkaline earth metal or ammonium. Typical examples are the carboxymethylation products of hexylmethyl amine, hexyldimethyl amine, octyldimethyl amine, decyldimethyl amine, dodecylmethyl amine, dodecyldimethyl amine, dodecylethylmethyl amine,  $\text{C}_{12/14}$  cocoalkyldimethyl amine, myristyldimethyl amine, cetyldimethyl amine, stearyldimethyl amine, stearylethylmethyl amine, oleyldimethyl amine,  $\text{C}_{16/18}$  tallowalkyl dimethyl amine and technical mixtures thereof.

Also suitable are carboxyalkylation products of amidoamines corresponding to formula (II):



in which  $\text{R}^4\text{CO}$  is an aliphatic acyl group containing 6 to 22 carbon atoms and 0 or 1 to 3 double bonds,  $\text{R}^5$  is hydrogen or represents alkyl groups containing 1 to 4 carbon atoms,  $\text{R}^6$  represents alkyl groups containing 1 to 4 carbon atoms,  $q_2$  is a number of 1 to 6,  $q_3$  is a number of 1 to 3 and Z is again an alkali metal and/or alkaline earth metal or ammonium. Typical examples are reaction products of fatty acids containing 6 to 22 carbon atoms, namely caproic acid, caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, palmitoleic acid, stearic acid, isostearic acid, oleic acid, elaidic acid, petroselic acid, linoleic acid, linolenic acid, elaeostearic acid, arachic acid, gadoleic acid, behenic acid and erucic acid and technical mixtures thereof, with N,N-dimethylaminoethyl amine, N,N-dimethylaminopropyl amine, N,N-diethylaminoethyl amine and N,N-diethylaminopropyl amine which are condensed with sodium chloroacetate. A condensation product of  $\text{C}_{8/18}$ -cocofatty acid-N,N-dimethylaminopropyl amide with sodium chloroacetate is preferably used.

Imidazolinium betaines may also be used. These compounds are also known compounds which may be obtained, for example, by cyclizing condensation of 1 or 2 mol fatty acid with polyfunctional amines such as, for example, aminoethyl ethanolamine, (AEEA) or diethylenetriamine. The corresponding carboxyalkylation products are mixtures of different open-chain betaines. Typical examples are condensation products of the fatty acids mentioned above with AEEA, preferably imidazolines based on lauric

acid or - again - C<sub>12/14</sub> cocofatty acid which are subsequently betainized with sodium chloroacetate.

#### Alkali metal sulfates

- 5           The alkali metal sulfates are typical inorganic salts such as, for example, potassium or sodium sulfate and mixtures thereof. The use of sodium sulfate is preferred for reasons of price and availability.

#### Preparations

- 10           Surface-active preparations in the context of the present invention are understood to be the water-containing pastes of the amphoteric or zwitterionic surfactants as such. More particularly, they contain no other surface-active substances, but – from their production – electrolyte salts, more particularly sodium chloride, unreacted starting materials and
- 15           optionally small quantities of free fatty acids or salts thereof. The preparations may be alkaline or acidic, i.e. they have a pH of typically 6 to 9 or 1 to 6. The content of amphoteric or zwitterionic surfactants, which is referred to as the “active substance content”, may be in the range from 25 to 55% by weight, based on the preparation, and is generally in the range
- 20           from 35 to 45% by weight. By contrast, the content of alkali metal sulfate may be between 0.01 and 5% by weight and is preferably between 0.1 and 3% by weight and more particularly between 0.5 and 1% by weight, again based on the preparation. The quantity of other ingredients (which do not contribute to the surface-active character of the preparation), more
- 25           especially electrolyte salts, such as sodium chloride, is typically between 5 and 10% by weight. This results in a typical water content of ca. 35 to ca. 60% by weight and, more particularly, 40 to 50% by weight. The Brookfield viscosity of such preparations (as measured in an RVT viscosimeter at 20°C, spindle 1, 10 r.p.m.) is less than 5,000 mPas and preferably in the
- 30           range from 1,000 to 2,500 mPas.

### Production process

A particular advantage of the present invention is that the alkali metal sulfates may be added both during and after production. Addition  
5 after production may be preferred in cases where the paste viscosity is to be adjusted to a very precise value. Accordingly, the present invention also relates to a process for the production of concentrated, low-viscosity surface-active preparations which is characterized in that fatty amines or fatty acid amidoamines are betainized with halocarboxylic acids or alkali  
10 metal salts thereof in known manner in the presence of alkali metal sulfates. So far as the betainization reaction is concerned, reference is specifically made to the disclosures of the prior-art publications cited above, so that there is no need for them to be repeated at length here. Alternatively, the present invention also relates to a second process for the  
15 production of concentrated, low-viscosity surface-active preparations which is characterized in that alkali metal sulfates are added to water-containing pastes of alkyl betaines and/or alkyl amidobetaines. As explained above, the quantity of alkali metal sulfates is calculated so that their content in the final preparations is from 0.01 to 5% by weight, preferably from 0.1 to 3%  
20 by weight and more particularly from 0.5 to 1% by weight.

### Commercial Applications

The addition of alkali metal sulfates, more especially sodium sulfate, even in very small quantities, is particularly suitable for reducing the  
25 viscosity of highly concentrated, for example – based on active substance – 35 to 45% by weight alkyl betaine or alkyl amidobetaine pastes to such an extent that they can be pumped and transported without difficulty. It does not matter whether the alkali metal sulfates are added during or after the production process. Accordingly, the present invention also relates to the  
30 use of alkali metal sulfates for reducing the viscosity of concentrated

aqueous preparations of amphoteric or zwitterionic surfactants, the quantity added – based on the preparations – being from 0.01 to 5% by weight, preferably from 0.1 to 3% by weight and more particularly from 0.5 to 1% by weight. The concentrates thus obtained are suitable, for example, for  
5 the production of manual dishwashing detergents or hair shampoos in which they may be present, for example, in quantities of 1 to 15% by weight and more particularly 3 to 8% by weight.

### Examples

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#### Comparison Example 1

1083 g (5.3 mol) of a hydrogenated cocofatty acid and 552 g (5.4 mol) of N,N-dimethyl aminopropylamine were introduced into a 2-liter four-necked flask equipped with a thermometer, condenser, water separator,  
15 nitrogen inlet pipe and stirrer and heated under nitrogen to 180°C. The water of condensation was continuously removed from the reaction vessel. The reaction was continued until the acid value of the mixture had fallen below 5. Excess amine was then removed in vacuo. 1500 g of cocofatty acid amidopropyl dimethylamine were obtained in this way and were  
20 adjusted with water to an active-substance concentration of 45% by weight. The preparation was virtually solid.

#### Example 1

Comparison Example 1 was repeated, except that the reaction of the  
25 cocofatty acid with the N,N-dimethyl aminopropylamine was carried out in the presence of 7.5 g (corresponding to 0.5% by weight, based on the final composition) of sodium sulfate. The mixture was again adjusted with water to an active substance concentration of 45% by weight and had a Brookfield viscosity (20°C, spindle 1, 10 r.p.m.) of 4,500 mPas.

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**Examples 2 and 3, Comparison Example C2**

Quantities of 0.5% by weight and 1% by weight of sodium sulfate were subsequently added to an aqueous preparation of cocamidopropyl betaine (Dehyton® PK, Cognis) with an active substance concentration of 45% by weight. The appearance and the viscosity of the pastes were then determined at 5, 10, 15 and 25°C. The results are set out in Table 1.

**Table 1****Appearance and viscosity of cocamidopropyl betaine pastes**

	Quantity of sodium sulfate added [% by weight]		
	None	0.5	1.0
<b>Appearance</b>			
- at 25°C	Gelled	Thinly liquid, cloudy	Thinly liquid, clear
- at 15°C	Gelled	Liquid, cloudy	Thinly liquid, clear
- at 10°C	Solid	Viscous	Thinly liquid, clear
- at 5°C	Solid	Solid	Thinly liquid, clear
<b>Viscosity [mPas]</b>			
- at 25°C	Gelled		< 3,000
- at 15°C	Gelled		< 3,000
- at 10°C	Solid		< 3,000
- at 5°C	Solid		< 3,000